PTO 09-3531

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1306004

PROCESS FOR OBTAINING NANOPOROUS SEMICRYSTALLINE POLYMERIC MATERIALS FROM SYNDIOTACTIC POLYSTYRENE IN A COMPLETELY EMPTY FORM USING LIQUID OR SUPERCRITICAL CARBON DIOXIDE

[Processo per l'ottenimento di materiali polimerici semicristallini nonoporosi a base di polistirene sindiotattico in forma completamente vuota mediante l'uso di anidride carbonica liquida o supercritica]

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UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. MARCH 2009
TRANSLATED BY: THE MCELROY TRANSLATION COMPANY

PUBLICATION COUNTRY	(19):	IT
DOCUMENT NUMBER	(11):	1306004
DOCUMENT KIND	(12):	B1
PUBLICATION DATE	(43):	20010523
APPLICATION NUMBER	(21):	SA98A/000008
APPLICATION DATE	(22):	19980616
INTERNATIONAL CLASSIFICATION	(51):	C 08 L
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TITLE	(54):	PROCESS FOR OBTAINING NANOPOROUS SEMICRYSTALLINE POLYMERIC MATERIALS FROM SYNDIOTACTIC POLYSTYRENE IN A COMPLETELY EMPTY FORM USING LIQUID OR SUPERCRITICAL CARBON DIOXIDE
FOREIGN TITLE	[54A]:	Processo per l'ottenimento di materiali polimerici semicristallini nonoporosi a base di polistirene sindiotattico in forma completamente vuota mediante l'uso di anidride carbonica liquida o supercritica

The invention concerns a process for obtaining nanoporous semicrystalline polymeric materials /1*
from syndiotactic polystyrene able to absorb, in the crystalline phase (lattice), liquid-or gaseous-phase volatile organic compounds even when these are under low concentration conditions.

Syndiotactic polystyrene is understood to be the polymer in which the syndiotactic structure is presented for at least long stretches of chain, allowing crystallization in the nanoporous form. Such polymer is obtained, for example, according to the method described in European Patent Application /2
No. 0271875 – Himont Italia.

The definition also includes styrene copolymers with a prevalently syndiotactic microstructure that can be crystallized into the nanoporous crystalline form with CH_2=CH-R olefins, in which R is an alkyl-aryl or a substituted aryl containing 6-20 carbon atoms, or with other copolymerizable ethylenically unsaturated monomers.

The invention belongs to the technical-scientific field of industrial chemistry, more particularly to the sector concerned with the separation of different types of molecules. It has industrial applications in the field of water treatment, wastewater, air pollution control and any situation that requires separating different types of molecules.

It is known that syndiotactic polystyrene (s-PS) is a semicrystalline thermoplastic polymeric material with an extremely complex polymorphism.

In particular, two crystalline forms (α and β) are characterized by planar zig-zag chain shapes, while two others (γ and δ) are characterized by chains with *s*(2/1)2-type spiral shapes.

It is further known that the δ form, which is obtained by crystallization in solution processes or treatments with other s-PS crystalline forms, is a lattice form, that is, the crystalline lattice includes low-molecular-weight host molecules; therefore its fine structure and X-ray diffraction spectrum depend on the type and the amount of host molecules included in the crystalline phase.

* [Numbers in right margin indicate pagination of the original text.]

A nanoporous crystalline form of s-PS was recently described, which is obtained by removing host molecules from the δ form and is therefore identified as an empty δ form (δ_v).

As described in Italian patent application No. RM94A000030, the δ_v form is characterized by X-ray diffraction spectra that are different from the starting lattice δ forms. In particular, regardless of the nature of the host molecules in the starting lattice structure, the δ_v form is characterized by an X-ray diffraction spectrum having reflections with greater intensity at 2θ (CuKα), equal to approximately 8.4°, 10.6°, 13.6°, 17.2°, 20.8° and 23.6°, with an intensity ratio between the two I(8.4°)/I(10.6°) peaks in the 5-9 interval. This last ratio in the lattice forms is decidedly lower and generally within the 0.2-3 interval.

The δ_v is able to absorb, from liquid or gaseous mixtures, in its crystalline phase (that is, to form /4
lattices with) volatile organic compounds, even when the latter are under low concentration conditions. Volatile organic compounds that can be absorbed are, for example, halogenated compounds (chloroform, methylene chloride, carbon tetrachloride, dichloroethane, trichloroethylene, tetrachloroethylene, dibromoethane, methyl iodide, etc.), aromatic compounds (benzene, toluene, styrene, etc.), cyclical compounds (cyclohexane, tetrahydrofuran, etc.) The liquid and gaseous mixtures from which such compounds can be absorbed may be based on water and air.

As described in Italian patent application No. RM94A000030, articles manufactured with the δ_v form are preferably obtained by washing articles of lattice δ form with suitable solvents or in gas streams, and solvents that may be used for washing are, for example, acetone and methyl-ethyl-ketone. Furthermore, according to said patent, articles manufactured with the δ_v form may also be obtained by treating lattice δ-form samples under high vacuum at temperatures lower than the polymer's vitreous transition temperature.

Such procedures allow articles to be obtained in δ_v form but with a host molecule content between 1 and 2% by weight. The residual host molecule content in the nanoporous material does not jeopardize /5

applicability to molecular separation processes that provide for absorbing molecules that are present in very low concentrations. It is noted, for example, that the maximum capacity of the nanoporous material for absorbing aromatic or halogenated organic compounds from aqueous solutions may reach values equal to or greater than 100% by weight in the case of high concentrations, but it is usually reduced to values below 10% by weight for concentrations below 10 ppm.

The procedures described above for obtaining the δ_v form, moreover, are not very efficient when host molecules are aromatic compounds such as toluene, *o*-dichloro-benzene and especially styrene, that is, the monomer from which syndiotactic polystyrene is obtained. In fact, in δ-form samples of syndiotactic polystyrene that lattice such aromatic compounds, both treatment with acetone or methyl-ethyl-ketone and thermal treatments under vacuum succeed in emptying the lattice δ form only after days of treatment, with the drawback of transforming it partly into the γ form, that is, into a non-nanoporous crystalline form. Styrene desorption from δ-form samples is especially relevant because such samples are obtained from polymerization processes performed in a liquid monomer. /6

This patent describes a process for obtaining and regenerating nanoporous semicrystalline polymeric materials based on syndiotactic polystyrene, in which the polymer is present in a completely empty crystalline form, characterized by the absence, in the X-ray diffraction spectra of disoriented samples, of peaks in the 2θ(CuKα) 10°-11° interval (Figure 1).

Moreover, this process is also efficient for emptying s-PS samples of lattice form that include strongly absorbed aromatic compounds such as toluene, styrene or *o*-dichloro-benzene, which cannot be emptied using the techniques described above without a partial transformation into the γ form.

The process includes extraction with carbon dioxide, either liquid or under supercritical conditions. In particular, the extraction temperature should be in the interval between room temperature and 120°C,

and the extraction pressure is chosen from the interval between 60 and 800 bar. The preferred extraction conditions used are $30°C < T < 70°C$ and $70 \text{ bar} < P < 150 \text{ bar}$.

With regard to methods based on extraction with liquid solvents, the method presented herein has the /7
advantage of being able to easily gather the host molecules desorbed from the lattice by decompressing the carbon dioxide, which, when transformed into gaseous conditions, loses its solvent power and can release the desorbed material into a suitable cooled separator.

For illustrative and non-limiting purposes, three examples of the process are described below.

Example 1

Syndiotactic polystyrene powder obtained by mass styrene polymerization is used. The powder thus obtained in the polymerization process is in lattice form, includes around 15% by weight of styrene and has an X-ray diffraction spectrum that shows an $I(\approx 8°)/I(\approx 10.5°)$ ratio equal to approximately 1.4 (Figure 2A).

After washing with boiling acetone for 48 h, the powder still contains 4% of low-molecular-weight substance and has an X-ray diffraction spectrum that shows an $I(8.4°)/I(10.6°)$ equal to approximately 5.5 (Figure 2B). Although the emptying of the δ lattice form of styrene is not complete, such diffraction figure has a peak at $2\theta \approx 9.5°$, which is typical of the γ crystalline form due to a partial transformation of /8
the δ form as a result of the performed treatment.

An extraction with carbon dioxide under supercritical conditions at $T = 40°C$ and $P = 200$ bar for 20 h, performed on the sample whose diffraction figure is shown in Figure 2A, allows a powder to be obtained in which the amount of residual styrene is less than 1% by weight and has an X-ray diffraction spectrum that does not show a peak at $2\theta \approx 10.5°$ or a peak at $2\theta \approx 9.5°$ (Figure 1).

Example 2

The same syndiotactic polystyrene powder used in Example 1 is employed. The powder thus obtained in the polymerization process is heated to 160°C. Said re-cooking process completely removes the styrene and induces a transition in the crystalline phase of the δ form (lattice) into the γ form. After treatment at reflux with toluene for 2 h, said powder assumes the lattice δ crystalline form, includes around 15% by weight of toluene and has an X-ray diffraction spectrum that shows an I(≈8°)/I(≈10.5°) ratio equal to approximately 2.0 (Figure 3A).

After washing with boiling acetone for 8 h, the powder has an X-ray diffraction spectrum that shows /9
an I(≈8°)/I(≈10.5°) ratio equal to approximately 3.7, indicating a partially filled δ form and a peak at $2\theta \approx 9.5°$, which indicates a partial transformation into the γ form (Figure 3B). Infrared spectroscopy measurements indicate that the δ form mainly lattices acetone molecules that can be removed by simple aeration for long times at ambient temperature or by heat treatment at 50°C. The X-ray diffraction spectrum of the sample emptied with acetone, after removing the acetone at 50°C, is shown in Figure 3C. Compared to the sample that still contains acetone (Figure 3B), said sample has the same amount of γ form, while the I(≈8°)/I(≈10.5°) ratio is greater than 10.

The same powder as in the δ form with toluene in Figure 2A following extraction with carbon dioxide under supercritical conditions at T = 40°C and P = 200 bar for 5 h, contains an amount of toluene that is less than 1% by weight and has an X-ray diffraction spectrum that is equal to that shown in Figure 1, which does not have peaks at $2\theta \approx 9.5$ and 10.5°.

Example 3 /10

Nanoporous material as obtained in Example 1 is used; its X-ray diffraction spectrum is shown in Figure 1. Following immersion for 5 min in water containing 100 ppm toluene, the nanoporous material

absorbs an amount of organic compound equal to approximately 7% its own weight and assumes an X-ray diffraction spectrum similar to that in Figure 3A, which shows an I(≈8°)/I(≈10.5°) ratio lower than 3.

The nanoporous material is regenerated, assuming an X-ray diffraction spectrum equal to that of the starting nanoporous material (Figure 1), following treatment with carbon dioxide under supercritical conditions at T = 40°C and P = 200 bar for 1 h.

Claims /11

1. Syndiotactic polystyrene-based materials, characterized by the fact that the polymer is substantially in a completely empty δ crystalline form, said crystalline form being characterized by an X-ray diffraction spectrum the intensity of reflections of which is greater at 2θ (CuKα), equal to approximately 8.4°, 13.6°, 17.2°, 20.8° and 23.6°, and which does not have peaks in the 10°-11° interval.

2. Syndiotactic polystyrene-based materials according to Claim 1, characterized by the fact that they can be successfully used for removing organic compounds from water and air, even when they are found in concentrations of below100 ppm.

3. Process for obtaining and regenerating syndiotactic polystyrene-based nanoporous materials according to Claims 1 and 2 that includes an extraction of the host molecules using carbon dioxide, preferably under supercritical conditions, from lattice δ-form samples.

4. Process according to Claim 3 that can empty δ-form samples when host molecules are aromatic /12 compounds such as toluene, *o*-dichloro-benzene and styrene.

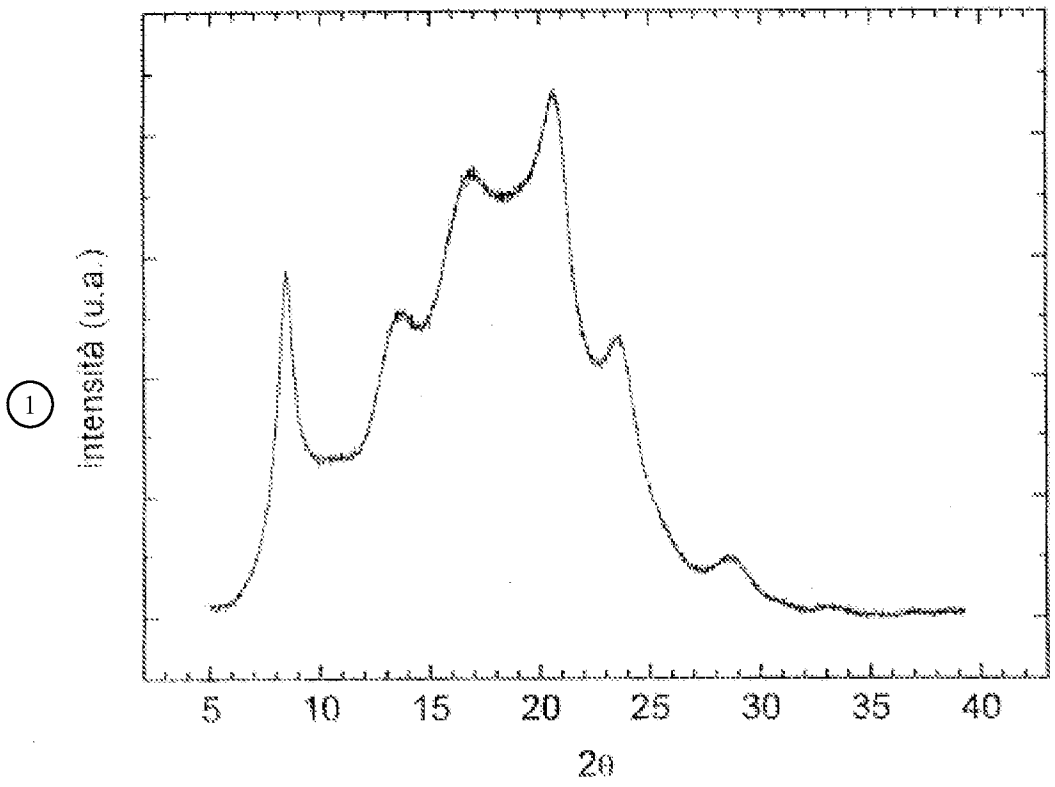

Figure 1

Key: 1 Intensity

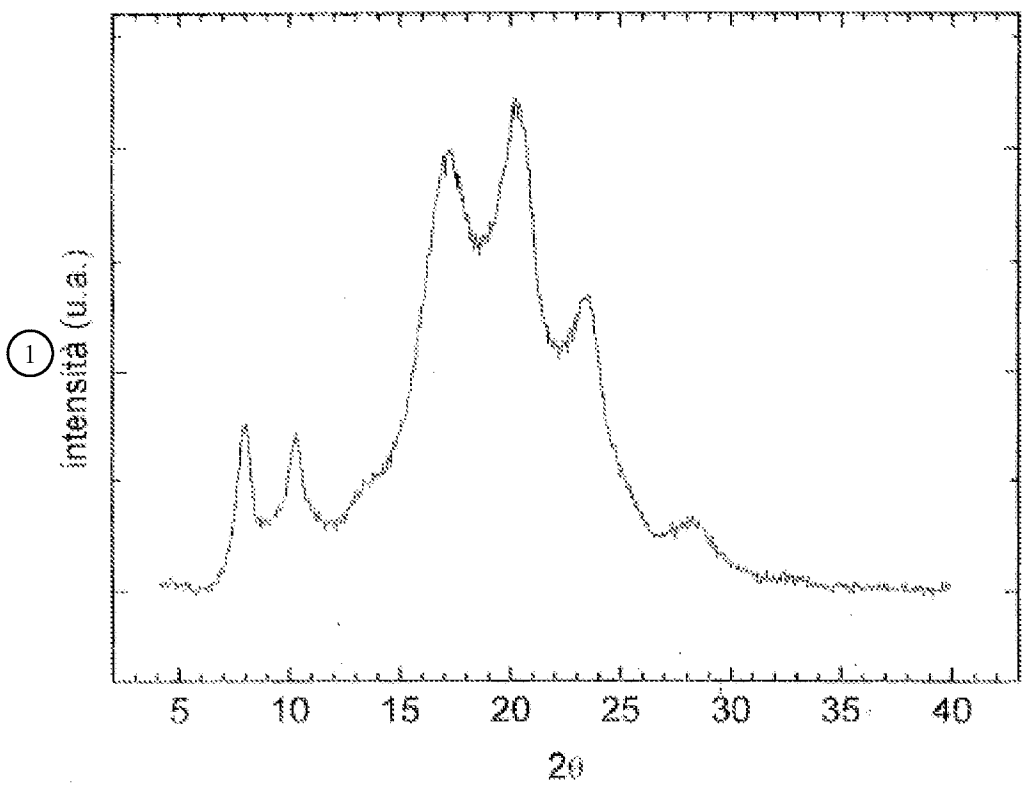

Figure 2A

Key: 1 Intensity

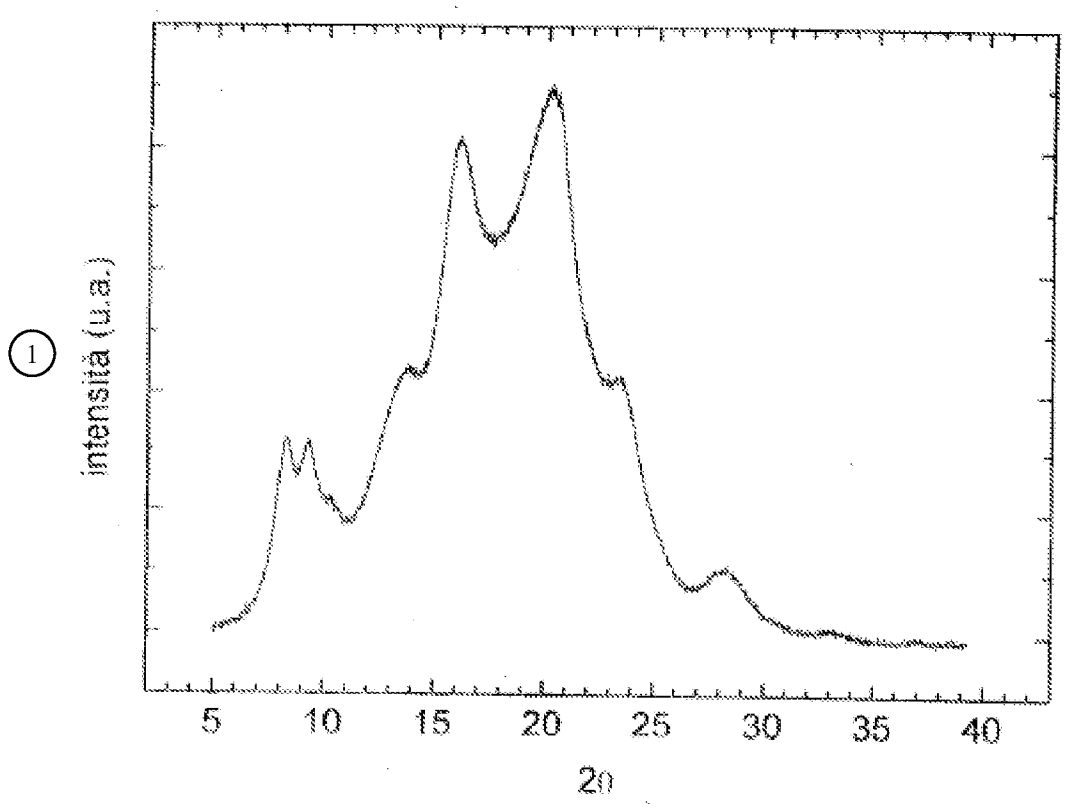

Figure 2B

Key: 1 Intensity

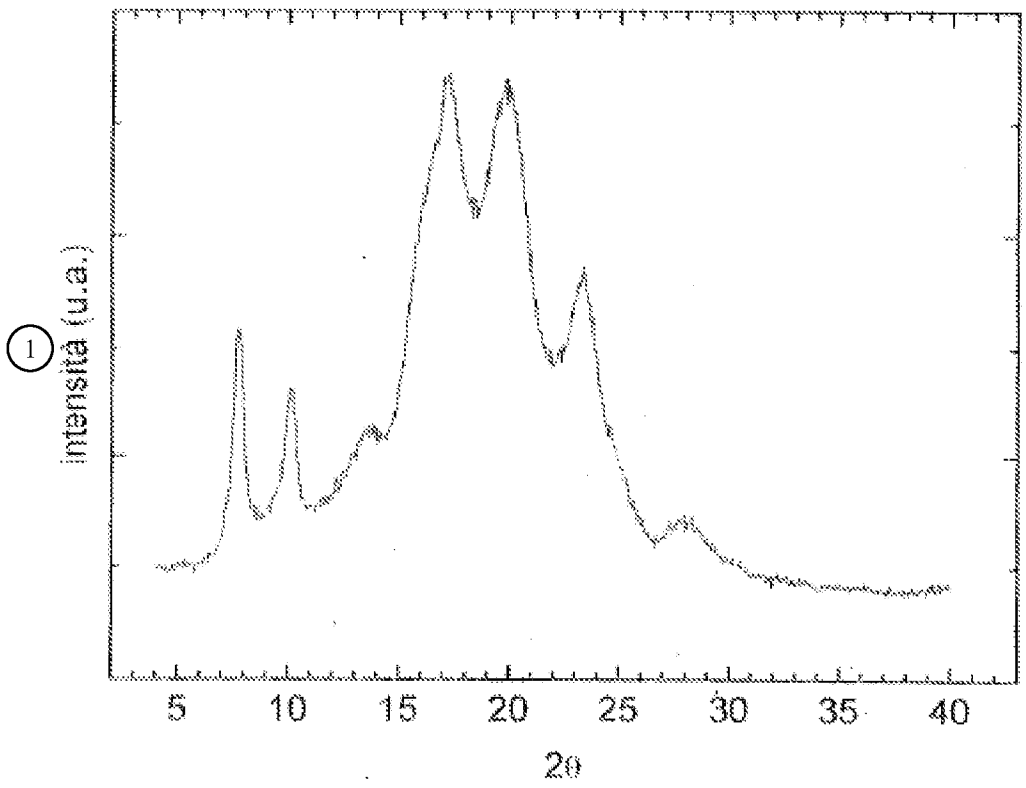

Figure 3A

Key: 1 Intensity

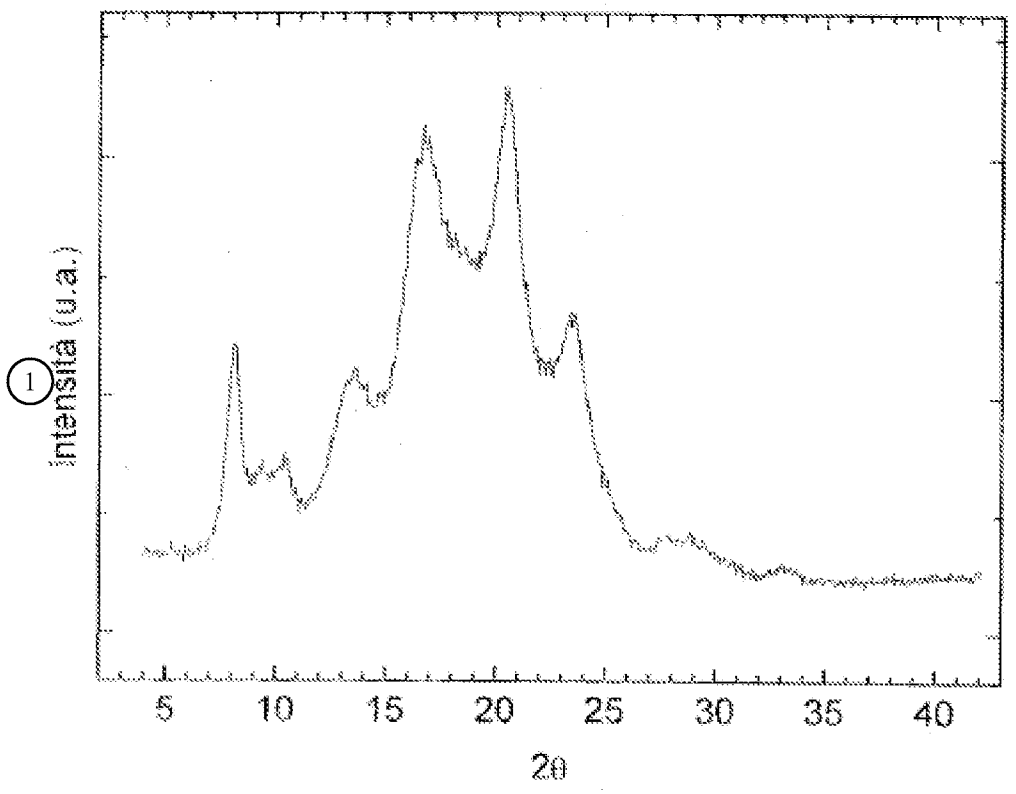

Figure 3B

Key: 1 Intensity

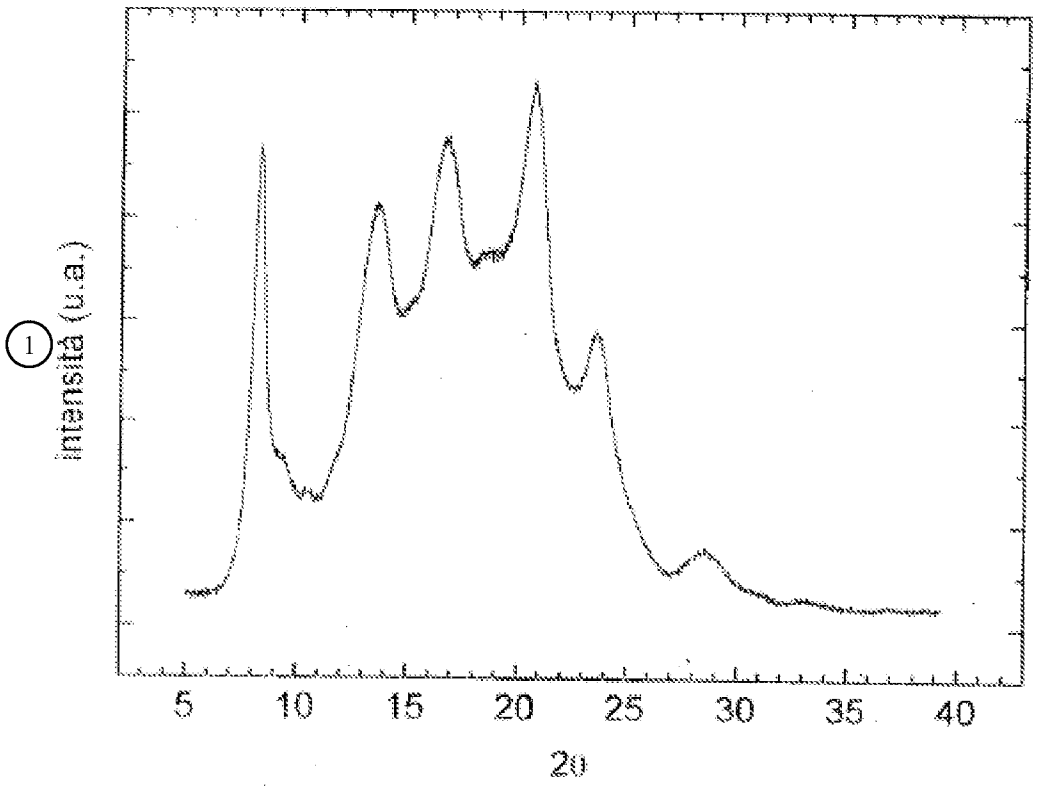

Figure 3C

Key: 1 Intensity